Mineralium Deposita (2018) 53:815–834
https://doi.org/10.1007/s00126-017-0782-0

ARTICLE

A new indicator mineral methodology based on a generic Bi-Pb-Te-S mineral inclusion signature in detrital gold from porphyry and low/intermediate sulfidation epithermal environments in Yukon Territory, Canada

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Received: 14 June 2017 / Accepted: 23 November 2017 / Published online: 22 December 2017

Abstract
Porphyry-epithermal and orogenic gold are two of the most important styles of gold-bearing mineralization within orogenic belts. Populations of detrital gold resulting from bulk erosion of such regions may exhibit a compositional continuum wherein Ag, Cu, and Hg in the gold alloy may vary across the full range exhibited by natural gold. This paper describes a new methodology whereby orogenic and porphyry-epithermal gold may be distinguished according to the mineralogy of microscopic inclusions observed within detrital gold particles. A total of 1459 gold grains from hypogene, eluvial, and placer environments around calc-alkaline porphyry deposits in Yukon (Nucleus-Revenue, Casino, Sonora Gulch, and Cyprus-Klaza) have been characterized in terms of their alloy compositions (Au, Ag, Cu, and Hg) and their inclusion mineralogy. Despite differences in the evolution of the different magmatic hydrothermal systems, the gold exhibits a clear Bi-Pb-Te-S mineralogy in the inclusion suite, a signature which is either extremely weak or (most commonly) absent in both Yukon orogenic gold and gold from orogenic settings worldwide. Generic systematic compositional changes in ore mineralogy previously identified across the porphyry-epithermal transition have been identified in the corresponding inclusion suites observed in samples from Yukon. However, the Bi-Te association repeatedly observed in gold from the porphyry mineralization persists into the epithermal environment. Ranges of P-T-X conditions are replicated in the geological environments which define generic styles of mineralization. These parameters influence both gold alloy composition and ore mineralogy, of which inclusion suites are a manifestation. Consequently, we propose that this methodology approach can underpin a widely applicable indicator methodology based on detrital gold.

Keywords Gold · Indicator mineral · Microchemical characterization · Porphyry systems

Introduction

Porphyry copper deposits have provided over 60% of global copper production and comprise over 70% of known reserves, with the importance of calc-alkalic porphyry deposits (Cu-Mo-Au) far exceeding that of alkalic Cu-Au systems (Mudd et al. 2013). Exploration for porphyry deposits whose outcrop is obscured by cover has encouraged the development of indicator mineral studies, in which dense and/or chemically stable minerals found in the erosional products of porphyry systems may be used to identify the presence of concealed hypogene mineralization (e.g., Averill 2011, Kelley et al. 2011, Eppinger et al. 2013). In British Columbia, this approach has been developed through study of trace element chemistry of specific rock-forming minerals, such as apatite (e.g., Bouzari et al. 2016; Mao et al. 2016), magnetite (e.g., Celis

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s00126-017-0782-0) contains supplementary material, which is available to authorized users.

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et al. 2014), and tourmaline (Chapman et al. 2015). At the supergiant Pebble Cu-Mo-Au deposit in Alaska, Kelley et al. (2011) characterized native gold distribution, grain size, and morphology both in hypogene ore and in the surficial environment, concluding that the distribution of gold and other resistate minerals (e.g., andradite and epidote) is a potentially useful vector to in situ mineralization. However, the authors noted that gold distribution considered in isolation was of limited value because populations of gold particles collected in the field could contain subpopulations from different sources. This scenario is commonly encountered in orogenic belts and a methodology which can distinguish between gold particles derived from different styles of mineralization would be advantageous. Here, we describe a study of gold signatures from the metallogenically complex Dawson Range in west central Yukon, which forms an ideal field laboratory for developing a generically applicable indicator methodology based on detrital gold grains.

The study area comprises a c. 250 × 40 km upland area stretching from south central Yukon WNW to the Alaskan border. It is primarily underlain by Palaeozoic metamorphic rocks of the Yukon-Tanana Terrane (YTT) that have been intruded by mid- to Late Cretaceous granitoids, or covered by their volcanic equivalents (Fig. 1). Both mid-Cretaceous and Late Cretaceous plutonic suites are associated with porphyry, skarn, and epithermal styles of mineralization, and orogenic gold is widespread in metamorphic rocks of the YTT (Allan et al. 2013). The exploration rush of 2009–2011 resulted in a number of discoveries in the Dawson Range, including the structurally hosted, 4.9 Moz Coffee gold deposit (Doerksen et al. 2016), the Klaza Au-Ag-Pb-Zn polymetallic vein deposit (1.35 Moz Au, 27 Moz Ag; Ross et al. 2016), as well as the definition of 2.8 Moz Au, 12.9 Moz Ag, and 189 × 10^3 T Cu at the previously discovered Nucleus and Revenue deposits (Armitage and Campbell 2011, Armitage et al. 2012). Additional gold discoveries in the adjacent White Gold district, such as the Golden Saddle orogenic gold deposit (1.3 Moz; Yukon MINFILE 115O 165) emphasize the strong regional variations in deposit style and ore controls in west-central Yukon (Allan et al. 2013). It is likely that gold from different styles of mineralization has contributed to the economically important placer deposits of Yukon (LeBarge 2007); although, in many cases, specific source-placer relationships remain unclear, as a consequence of lack of exposure of bedrock. The study of detrital gold provides an obvious strategy for exploration and metallogenic studies in the region.

Natural gold may be characterized according to the other elements present in the alloy (e.g., Knight et al. 1999) and the suite of mineral inclusions which are revealed in polished sections, (e.g., Chapman et al. 2000). Morrison et al. (1991) identified some broad differences in the compositional range of gold from different styles of mineralization; for example, epithermal mineralization may yield gold with a wide range of Au/Ag ratios, and gold from porphyry environments typically exhibits a slightly higher Cu content. Townley et al. (2003) undertook a wide-ranging study of gold compositions in porphyry Cu, porphyry Cu-Au, and epithermal mineralization. Ternary diagrams constructed to show Au- (Ag × 10) and (Cu × 100) depicted largely mutually exclusive compositional fields for each population. However, these compositional fields relate only to magmatic-hydrothermal systems and cannot be used to differentiate between the low-Cu epithermal signature of epithermal gold and that of gold derived from orogenic systems (Moles et al. 2013).

Characterization of inclusion assemblages in gold samples in conjunction with host alloy composition has yielded data sets defining the "microchemical signature" of a sample population. The microchemical signature may be applied to evaluate variation within a single style of mineralization in a specific area (e.g., Chapman et al. 2010a, b, Chapman and Mortensen 2016) or to investigate a specific signature associated with a particular style of Au mineralization (e.g., Chapman et al. 2009). This approach has proved particularly valuable in the study of gold from alkalic porphyry systems in which gold is precipitated in different hydrothermal settings within the evolving system (Chapman et al. 2017). In some cases, the ranges of alloy compositions of populations of gold grains from different styles of mineralization overlap, but the associated mineralogy represented in the inclusion assemblage may provide a useful discriminant.

The aims of the present study with respect to Yukon are threefold: (i) to compare microchemical signatures of gold derived from porphyry systems with those of orogenic gold, (ii) to investigate the evolution of microchemical signatures between porphyry and associated epithermal environments, (iii) to develop a methodology which can differentiate between gold derived from different deposit types in Yukon. All these elements contribute to a wider research remit which seeks to evaluate the potential for gold as an indicator mineral.

Geological setting

The Late Cretaceous Casino plutonic suite (79–72 Ma) is especially prospective for porphyry and epithermal styles of mineralization in the Dawson Range of west-central Yukon, examples of which are the basis of the present study. A summary of resource and placer production figures from these localities is presented in Table 1.

Nucleus and Revenue The Revenue and Nucleus deposits are two of several mineral occurrences of the Dawson Range that are spatially and structurally related to the strike-slip Big Creek fault system (Fig. 1). The Revenue Au-Ag-Cu-Mo deposit is centered on the Revenue breccia, a polyphase

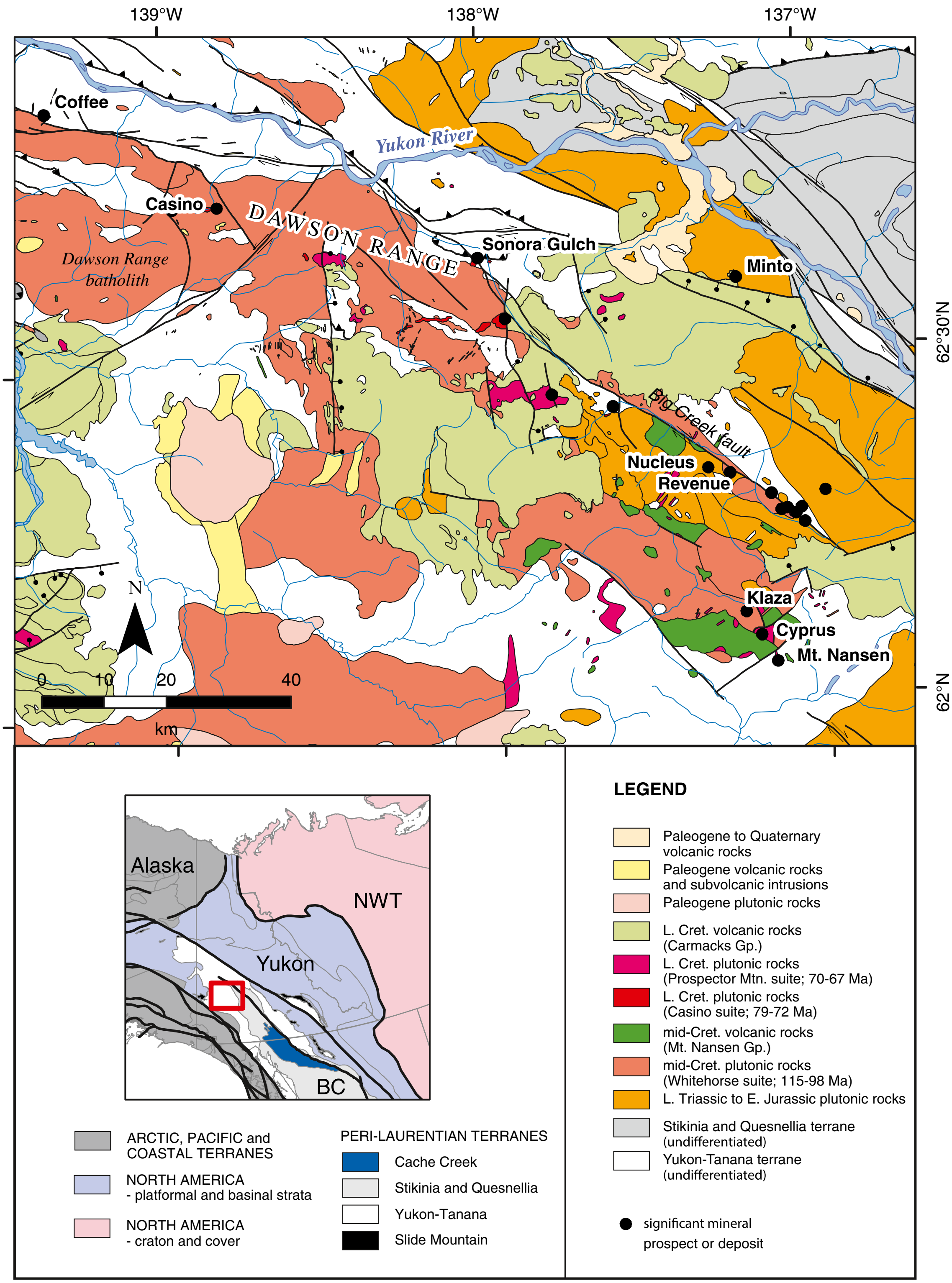

Fig. 1 Geology of the Dawson Range and location of the various study areas (after Yukon Geological Survey 2017)

porphyry-breccia complex intruding granitoids of the mid-Cretaceous Dawson Range batholith and metasedimentary rocks of the Yukon-Tanana terrane. The breccia is dominated by granitoid and porphyry clasts and is locally characterized by autobrecciated quartz-feldspar porphyry dikes that are Late Cretaceous (75.4 ± 0.5 Ma; Allan et al. 2013). Host rocks to the Revenue breccia were affected by an early phase of biotite ± K-feldspar ± magnetite alteration. K-feldspar alteration also affected the Revenue breccia and related porphyry dikes. Rocks within and adjacent to the Revenue breccia are

Table 1 Resource and production parameters of localities in this study

Deposit	Resource	Associated placer/eluvial occurrences	
		Localities	Production figures to 2007 (oz)[6]
Nucleus[1]	Indicated and inferred: 1.7 Moz Au, 2.7 Moz Ag, 58,967 t Cu;[1]	Mechanic Creek	2160
Revenue[2]	Inferred: 1.1 Moz Au, 10.2 Moz Ag, 130,181 t Cu, and 40,823 t Mo[1]	Revenue Creek and tributary (Whirlwind Creek)	9982
Casino[3]	Measured, indicated, inferred: 101 Mt containing 0.39 g/t Au (oxide gold zone), 87 Mt containing 0.25% Cu, 0.29 g/t Au, 0.02% Mo and 1.7 g/t Ag (supergene oxide enriched zone); 2700 Mt of sulfide ore containing 0.16% Cu, 0.19 g/t Au, 0.02% Mo and 1.5 g/t Ag (combined supergene sulfide and hypogene zone)	Canadian Creek and tributary (Potato Gulch)	16,917
Sonora Gulch[4]	No current resources; best intercept 25 g/t Au and 39 g/t Ag from 0.8 m ("Tetradymite vein")[4]	Sonora Gulch	30
Cyprus[5]	No current resources, but typical returns from trenches1-3 g/t Au (up to 11 g/t) and 10–15 g/t Ag; typical Cu grades 0.1–0.15%[5]	Discovery Creek	1580
		Nansen Creek	21,700
Klaza[5]	Inferred: 9.4 Mt containing 1.36 Moz Au at 4.48 g/t and 27.0 Moz Ag at 89.02 g/t[5]	Canaan Creek	NR

Locations of deposits illustrated in Fig. 1[1] Armitage and Campbell (2011); [2] Armitage et al. (2012); [3], Casselman and Brown (2017); [4] Yukon Geological Survey MINFILE; [5] Turner and Dumala (2017); [6] LeBarge (2007); NR = not recorded

overprinted by widespread sericitic alteration. The earliest recognized phase of hypogene mineralization in the Revenue breccia is cavity and fracture-filling chalcopyrite, pyrite, molybdenite, and minor scheelite and powellite. Highest Au grades correspond to a paragenetically later generation of veins and disseminations containing pyrrhotite, marcasite, arsenopyrite, and bismuth tellurides intergrown with microcrystalline pyrite. Kaolinite alteration, accompanied by azurite, malachite, tenorite and Fe-Mn oxides, is observed in the upper ~ 60 m of the Revenue deposit as the result of oxidation.

A broad, 2.5 × 6 km induced polarization chargeability anomaly surrounding the Revenue breccia (Armitage and Campbell 2011; ESM 1) corresponds to variably mineralized sericite-pyrite alteration where drill-tested. The Nucleus Au-Ag-Cu deposit represents a Au-rich domain at the western margin of the chargeability anomaly and is characterized by low-grade vein and disseminated mineralization hosted by metasedimentary rocks, mid-Cretaceous aplite, and Late Cretaceous porphyritic dikes (Allan et al. 2013). The Nucleus deposit also contains several high-grade zones of gold mineralization characterized by massive sulfides intergrown with amphibole (Betsi et al. 2016). Ore minerals at Nucleus include pyrite, chalcopyrite, arsenopyrite, pyrrhotite, marcasite, bismuth tellurides, and native gold. The bulk of mineralization at Nucleus is inferred to be age-equivalent to post-breccia Au mineralization at Revenue, based on common metal and mineral assemblages, textural properties, and the compositional similarity of placer gold (see below).

Sonora Gulch Sonora Gulch is a drill-tested cluster of porphyry and epithermal prospects associated with Late Cretaceous hypabyssal stocks and dikes of monzonitic composition (ca. 75–74 Ma; Bennett et al. 2009) that intrude Late Permian monzogranite orthogneiss, discontinuous lenses of serpentinized pyroxenite, and granitoids of the mid-Cretaceous Dawson Range batholith (Bennett et al. 2009; Ryan et al. 2013; Yukon MINFILE 115J 008) (ESM 2).

Several styles of mineralization have been described at Sonora Gulch. Porphyry-style Cu-Au mineralization is mainly associated with pyrite and chalcopyrite in disseminations and veinlets in Late Cretaceous intrusions. Several examples of precious metal-enriched veins are also described, including: (1) the "Tetradymite Vein"—a gold and tetradymite-bearing quartz vein system oriented parallel to the Big Creek fault; (2) Au-Ag-Pb-Sb-enriched polymetallic quartz-calcite-pyrite-boulangerite-bournonite veins cutting rhyolite porphyry bodies of probable Late Cretaceous age; (3) quartz-arsenopyrite ± sphalerite-galena-stibnite veins with anomalous Au values; (4) Au-enriched Cu-Zn-Pb skarns; (5) bonanza-style lode gold associated with listwaenite-altered ultramafic rocks (Bennett et al. 2009; Yukon MINFILE 115J 008).

Casino The Casino deposit consists of a weathered Cu-Au-Mo-Ag porphyry system that includes a near flat-lying oxidized leached cap, a supergene oxide zone, a supergene sulfide zone, and a large volume of underlying hypogene ore (Casselman and Brown 2017; ESM 3). The undeveloped deposit is within the Casino Complex, which comprises a pipe of brecciated granite of the mid-Cretaceous Dawson Range batholith, intruded by the Patton Porphyry, a Late Cretaceous (74.3 ± 0.5 Ma; Allan et al. 2013) stock of plagioclase-hornblende dacite to rhyodacite porphyry. Hypogene mineralization occurs as pyrite, chalcopyrite, molybdenite, and minor hübnerite, developed mainly in steep zones at the contact of the Patton Porphyry and surrounding breccia. Mineralization is associated with the margins of a 450 m-diameter potassic alteration zone, which transitions outward into sericite-pyrite alteration, and weakly developed argillic and propylitic alteration (Yukon MINFILE 115J 028). The oxidized leached cap is enriched in Au and depleted in Cu, whereas the supergene sulfide zone contains Cu grades typically double that of the hypogene zone (0.43 vs. 0.23%). The Casino deposit measures approximately 1.0 × 1.8 km in plan view, standing out by far as Yukon's largest porphyry deposit. Precious metal-enriched veins are also present in the Casino area and include the Ag-Pb-enriched Bomber occurrence (Yukon MINFILE 115J 027), and Au-enriched quartz-arsenopyrite-carbonate veins in the Canadian Creek area (Yukon MINFILE 115J 101).

Cyprus Cyprus is a drilled porphyry Cu-Au prospect located in the Mt. Nansen epithermal and placer district of the Dawson Range (Yukon MINFILE 115I 066) (Online Resource 4). Mineralization is hosted in quartz monzonite to granite porphyry plugs and dikes of Late Cretaceous age (76.0 ± 0.4 Ma; Mortensen et al. 2016), which intrude granodiorite of the mid-Cretaceous Dawson Range batholith (Hart and Langdon 1997). Hydrothermal breccia bodies with a quartz ± tourmaline cemented matrix have also been described, which are surrounded by zones of phyllic, argillic, and propylitic alteration (Yukon MINFILE 115I 066). Pyrite, chalcopyrite, and molybdenite occur in quartz-sulfide veinlets and as disseminations most abundant in the phyllic alteration zone. A supergene chalcocite zone developed below an approximately 60 m-thick leached cap results in enrichments of Cu up to 0.5–0.6%, compared to average hypogene Cu grades of 0.1–0.15%.

Klaza The Klaza Au-Ag-Zn-Pb deposit is located approximately 5 km northwest of the Cyprus porphyry prospect and is underlain mainly by granitoids of the Dawson Range batholith. The deposit comprises a set of northwest-trending polymetallic veins (e.g., the BRX and Klaza zones; ESM 4) of intermediate sulfidation epithermal character that are spatially and potentially genetically associated with a swarm of felsic to intermediate porphyry dikes of Late Cretaceous age (78.2–76.3 Ma; Mortensen et al. 2016). Mineralization occurs as veins, sheeted veinlets, and tabular breccia bodies, with a mineral assemblage of quartz, pyrite, arsenopyrite, galena, sphalerite, various sulfosalts, electrum, Mn-carbonate, and barite. A suite of magnetite-bearing, intermediate to mafic dikes also occurs closer to the Cyprus porphyry; these are also locally mineralized, hosting disseminated pyrite along with minor chalcopyrite and molybdenite (Mortensen et al. 2016).

Native gold in porphyry-epithermal systems

Gold in hypogene environments

Most gold within porphyry systems is associated with chalcopyrite and/or bornite in an ore zone hosted by potassically altered rocks, and this association has been the focus of most studies because of its economic dominance. Gold formed in the main ore stage of porphyry deposits in potassically altered rocks normally occurs as tiny (typically < 20 μm) exsolution blebs in bornite or chalcopyrite (e.g., Simon et al. 2000; Kesler et al. 2002; Arif and Baker 2004). Gold may also occur in quartz; for example, Bower et al. (1995) reported that gold particle size at Casino is smaller (c. 15 μm) in chalcopyrite than in quartz (50–70 μm), and Arif and Baker (2004) reported a similar size relationship at the Batu Hijau porphyry Cu-Au deposit in Indonesia, whilst noting that gold grains associated with quartz were compositionally distinct from those closely associated with sulfides. Sillitoe (2000) reports that native gold in porphyry systems is in general >'800 fine' (i.e., >80 wt% Au) but more detailed consideration of the variation of gold mineralogy within the evolving system is required to underpin an indicator-based exploration methodology.

Despite the economic importance of gold within the potassic zone, gold from other environments within the evolving magmatic hydrothermal system may be important in the context of developing an indicator mineral methodology. An assessment of the range of depositional environments and the nature of associated gold mineralization is provided below.

Assemblages of alteration minerals are generated by broad changes in P-T-X conditions which are replicated at different porphyry deposits. An obvious approach to characterizing gold within porphyry systems would involve establishing compositional signatures corresponding to the alteration assemblages within the host rocks. The basis for this is that gold composition is a function of the same parameters which govern alteration, but permissible conditions in the propylytic and phyllic regimes encompass environments in which gold may either be precipitated or dissolved. For example, Gammons and Williams-Jones (1997) describe the stripping of gold from pre-existing auriferous chalcopyrite-bornite ore and both Bower et al. (1995) and Hart and Langdon (1997) observed the removal of both Au and Cu during the phyllic overprint of the potassic zone at Casino and Cyprus, respectively. Elsewhere Palacios et al. (2001) reported gold associated with sericitic (phyllic) veins at Cerro Casale, and Chapman et al. (2017) identified gold grains in propylitically altered rocks at the Mount Milligan alkalic porphyry in British Columbia. In some cases, the Ag content of gold alloy decreases with successive alteration environments (e.g., Cerro Casale: Palacios et al. 2001; Pebble, Alaska: Gregory et al. 2013), whereas in other cases, the opposite trend has been recorded (e.g., Santo

Tomas II, Philippines: Tarkian and Koopmann 1995; Circle City: Antweiler and Campbell 1977).

Gammons and Williams-Jones (1995) identified the parameters which control Au/Ag ratios in gold alloy which provide a framework for interpreting empirical data. If, as many authors suggest, Au is transported as a hydrosulfide complexes and Ag as a chloride complex, the generic controls on gold alloy composition are temperature, $(Au/Ag)_{(aq)}$, $aCl^{-}_{(aq)}$, $aH^{+}_{(aq)}$, and $aH_2S_{(aq)}$. In zones of propylytic and phyllic alteration, Au-bearing fluids generated by remobilization of pre-existing mineralization inherit the Au/Ag ratio of that ore. The composition of gold formed in subsequent mineralizing environments may vary according to prevailing conditions. Most importantly, lower temperatures (potassic-propylitic transition) correlate with lower Au/Ag ratios in the alloy, whereas the lower pH (propylitic-phyllic transition) acts to lower the Ag content. Progressive lowering of both $Au/Ag_{(aq)}$ and $aH2S_{(aq)}$ inevitably accompany mineral precipitation and these act to reduce and raise Au/Ag_{alloy}, respectively. Finally, the alloy composition may also be influenced according to Ag speciation in the presence of Te and Se (Morrison et al. 1991), which may be important at locations where telluride minerals are observed as inclusions within gold particles.

Given that such major differences in Au behavior are possible at different localities within parallel alteration assemblages, it seems highly unlikely that it will be possible to construct a simple generic template relating gold compositional to alteration zone.

Sillitoe (2010) reported late stage "subepithermal" base metal veins as a common feature of porphyry systems. LeFort et al. (2011) concluded that Au-bearing veins of the alkalic porphyry at Mt. Milligan, B.C., constituted an example of this relationship. Chapman et al. (2017) suggested that the majority of gold grains in the placer environment local to alkalic porphyry deposits in British Columbia were derived from such late stage veins. Corbett and Leach (1995) described vertical zonation in low sulfidation epithermal systems from deeper Au-Cu-dominated mineralogy to shallower, later Au-Ag mineralization, and it seems probable that the microchemical signatures of gold from such low sulfidation environments would be sympathetic to this compositional progression.

Some generalizations may be made concerning the mineralizing environments present within low sulfidation epithermal systems with respect to the prevailing conditions within the phyllic (i.e., later stage) environment of a porphyry system. Firstly, Au is transported as a hydrosulfide complex and Ag as a chloride complex; secondly, low sulfidation environments are much cooler than those associated with the porphyry systems; and thirdly they also form at near-neutral pH. All these factors favor precipitation of relatively high Ag alloy (Gammons and Williams-Jones 1995). In addition, a wider range of P-T-X variation is commonly associated with epithermal systems. Consequently, the generic observations of Morrison et al. (1991) describing gold from epithermal environments as exhibiting variable, but generally high Ag contents, are consistent with considerations of the controls on alloy composition proposed by Gammons and Williams-Jones (1995).

The intimate association of gold with bismuth-bearing minerals at Nucleus and Revenue could be a consequence of Au scavenging by liquid bismuth-bearing phases; i.e., an example of the 'bismuth collector' model (Tooth et al. 2008). Mineralogical association in a variety of ore deposit styles have been ascribed to this process; Au skarns (Cockerton and Tomkins 2012), massive sulfide deposits (Törmänen and Koski 2005), epithermal systems (Cook and Ciobanu 2004) and orogenic deposits of different ages (e.g., Oberthür and Weiser 2000, Ciobanu et al. 2010). Most studies have focused on Au-Bi systems and identify conditions in which gold may be assimilated into a melt. Whilst one inclusion of native bismuth was observed in a gold particle from Revenue Creek (Fig. 2a), the main association is Au-Bi-Te ± S, which has been observed repeatedly both in detrital grains and in situ mineralization (e.g., Figs. 2b and 5b). Ciobanu et al. (2005) suggest that bismuth telluride melts may also scavenge Au from hydrothermal solutions and also note that varying degrees of substitution of S and Se for Te are likely. In the present study the Bi-sulfotelluride-gold association is common, and in addition Sb and Pb were commonly detectable. Cook and Ciobanu (2004) also report substitution of Pb for Bi in Bi-Te-S minerals from the porphyry stage mineralization in the Larga-Fața Báii field, Metaliferi Mountains, Romania. In conclusion, the bismuth telluride collector model may play a role in the formation of gold particles at Nucleus/Revenue, and this possibility is explored further in the context of our results in a later section.

Detrital gold derived from porphyry-epithermal systems

Gold particles eroded from Cu-Au porphyry systems will inevitably be present in the surficial environment and in a few cases they are present in sufficient concentrations to form an economically viable placer deposit (e.g., the Revenue, Mechanic and Canadian creeks discussed in the present contribution). Gold particles hosted by potassically altered rocks are commonly 10-50 μm in size and only the largest of these can be isolated by hand panning. Therefore sample populations of detrital gold collected from the environs of porphyry systems are most likely to represent later stage vein and epithermal mineralization. Despite the potential for loss of fine gold from the local fluvial sediments through winnowing, placer production, figures can provide a useful indication of the Au tenor of a porphyry–epithermal system and data relating to placers in the study areas have been included in Table 1.

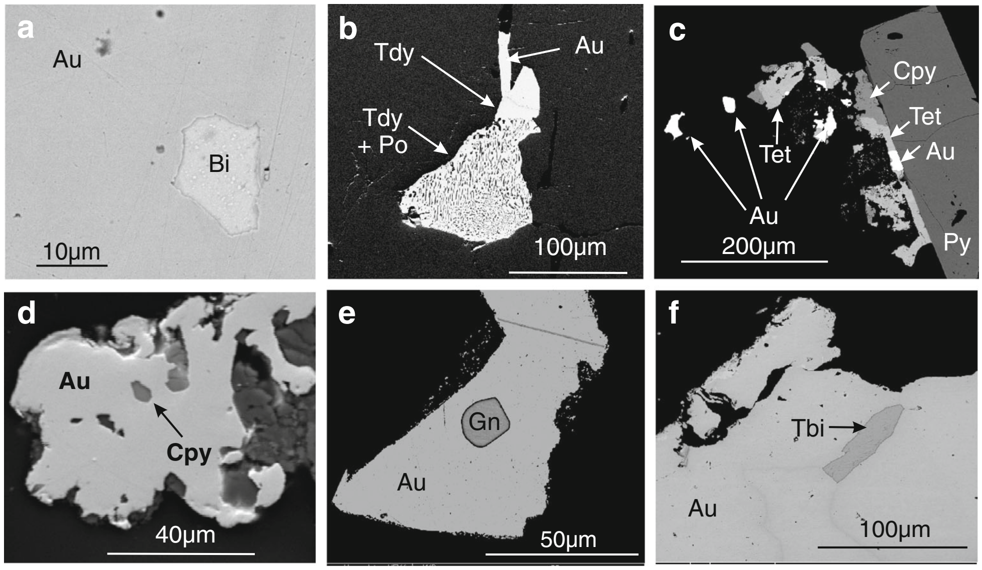

Fig. 2 Context and textures of in situ, eluvial and placer gold grains. **a** Native bismuth inclusion in gold grain from Revenue Creek; **b** Au-Bi-telluride- pyrrhotite association in hypogene sample from Nucleus; **c** chalcopyrite, gold, and sulfosalts postdate pyrite (hypogene ore, Casino); **d** eluvial gold grain from Casino; **e** galena inclusion in eluvial grain from BRX-1, Klaza; **f** Bi telluride inclusion in placer grain from Canadian Creek; mineral name abbreviations as in Table 3, plus Tdy = tetradymite (Bi_2Te_2S)

Methodology

General approach

The overall approach of this study is to establish clear compositional signatures and mineral associations of native gold in hypogene porphyry or epithermal systems, and to compare these with the microchemical signature of particulate gold from both eluvial and local placer environments. The term 'sample population' herein refers to a number of gold grains collected at a single locality. The size of the populations are indicated in Table 2, and the relationships between specific porphyry systems and associated placer localities are specified in Table 3. In this approach two important criteria must be considered. Firstly, it is necessary to establish that hypogene gold grains are unmodified in the surface environment. In practice this is achieved during the characterization process through inspection of sections of gold grains. The subject of gold grain modification in the surficial environment in the context of gold particle characterization is discussed in detail in Chapman et al. (2011), who strongly advocate a purely detrital origin for the many thousands of gold particles studied in this way. Secondly, sample populations of detrital grains may contain particles derived from different sources. Chapman and Mortensen (2016) noted that gold grains collected from allochthonous placer deposits may be derived from multiple sources, whereas autochthonous placers are typically associated with smaller catchments and are more likely

Table 2 Characteristics of gold grains from hypogene, eluvial and placer environments. Abbreviations: M= max value, C= % of population containing detectable Cu or Hg. Mineral abbreviations: Apy = arsenopyrite, bd= below detection, Bis= Bismuthinite, BiTe = bismuth tellurides, BiTe(S) = bismuth sufotellurides, Cpy= chalcopyrite, Gn= galena, Na= Not analysed, Po= pyrrhotite, Py= pyrite, Sph= sphalerite, Tet= tetrahedrite

	Au grains	Sample source		Ore mineral association	Cu		Hg	
					M	C	M	C
Nucleus	5	Hole X109 depth 113.3 m GRD08–099 Hole X116 depth 116 m GRD08–099		BiTe(S), Po	0.12	100	0	0
Casino	12	Hole CAS 060, interval 160- 163 m, Potassic zone		Gn, Bis, Tet, Cpy	0.7	67	0	0
Klaza	8	Hole KL-11-33 depth 121- 122 m Hole KL-12-96 depth 343-346 m			bd	0	0.26	100
BRX-1	63	382,410	6,889,676	Py, BiTe ii. Gn, Po, Sph, Cpy, Apy	bd	0	0.55	86
BRX-2	114	381,715	6,890,310	i. Py, BiTe ii. Gn, Po, Sph, Cpy, Apy	bd	0	0.27	96

to contain gold from a single source (e.g., Chapman et al. 2010a).

Location maps indicating the sampling sites at Casino, Klaza and Nucleus-Revenue are provided in the Online Resources 1–4. Samples of in situ mineralization were available from previous studies and these are described in Table 2. Eluvial samples were collected from decomposed surface mineralization at Casino and Klaza by Chapman et al. (2014, 2016), respectively. The material was processed using a portable sluice, and gold grains were subsequently isolated from the sluice concentrates by picking under a binocular microscope.

Sampling localities for placer gold grains were chosen in order to aid subsequent considerations of placer-lode relationships. For example, at Revenue and Nucleus, the hypogene mineralization lies within the catchment area of Revenue and Mechanic creeks, respectively. In these cases multiple sample populations of placer gold were collected such that any zonation in hypogene mineralization would be reflected in corresponding spatial variation in the respective microchemical signatures of the placer gold populations. In the Cyprus-Klaza area samples were collected both from tiny catchments such as Canaan and Discovery creeks to constrain the potential contributing sources, whereas a composite sample was obtained from contiguous placer mining claims in the trunk drainage of Nansen Creek (Online Resource 4). Large sample populations such as this are useful because they permit evaluation of the relative importance of gold from different sources.

Collection of placer samples was undertaken using specialized field techniques developed for efficient collection of sample populations in areas of low gold grain abundance (as described by Leake et al. 1997), which involves either panning or sluicing of fluvial gravel. Gold grains were recovered from sluice concentrates by hand panning. Gold from previous studies was also available and the details of sample origins are indicated in Table 3.

Analytical methods

The sample populations from upper Revenue and Whirlwind creeks comprise both particles collected during the present study and others from nearby localities which were part of a collection at UBC. Alloy compositions of gold from the UBC collections were previously determined in Vancouver (J. Knight, unpublished data), whereas the suite of mineral inclusions was established at the University of Leeds (UoL) as part of the present study.

Populations of placer gold particles were mounted for polishing according to size, as described by Chapman et al. (2000). Quantitative compositional characterization of the gold particles was carried at UBC using a Cameca SX50

Table 3 Gold grains from placer/eluvial environments. Indices refer to derivation of samples: [1] =Wrighton (2013), [2] = UBC collections, (EMP data courtesy of John Knight), [3] = Chapman et al. (2014), [4] = Chapman et al. (2016), [(i)] and [(ii)] indicates sample data combined as indicated for subsequent comparisons

Locality	Drainage	Latitude WGS84	Longitude WGS84	No of particles	Minor alloying elements			
					Cu		Hg	
					M	C	M	C
Nucleus/revenue	Revenue left Fork [1]	62.33599	− 137.27503	163	0.1	71	1.1	2.1
	Whirlwind Ck[1]	62.33548	− 137.27611	65	0.08	80	0.3	1
	Upper Revenue Ck [2(i)]	62.33543	− 137.27487	64	Na	Na	Na	Na
	Lower Revenue Ck[1(i)]	62.34013	− 137.27517	102	0.08	75	0	0
	Upper Mechanic[1]	62.32856	− 137.31399	144	0.08	83	0	0
	Mid Mechanic Ck[1(ii)]	62.33946	− 137.31271	34	0.08	68	0	0
	Lower Mechanic Ck[1(ii)]	62.34813	− 137.30377	38	0.07	84	0.9	3
Sonora Gulch				8	0.07	88	0	0
Casino	Leached cap (eluvial)[3]	62.73827	− 138.83003	34	0.15	97	0	0
	Canadian Ck[3]	62.74511	− 138.84821	134	0.19	95	0	0
	Potato Gulch[3]	62.79859	− 138.81341	38	0.05	89	2.2	11
		62.08286	− 137.17276					
Cyprus/Klaza	Nansen Ck[4,5]	62.13608	− 137.27441	157	0.15	50	0.38	100
	Discovery Ck [4]	62.12074	− 137.25431	102	0.13	80	0.36	100
	Canaan Ck.[4]	62.12621	− 137.26805	104	0.07	41	1.14	100
	BRX 1 (eluvial)[4]	62.73827	− 138.83003	63	0.66	35	0.61	87
	BRX 2 (eluvial)[4]	62.74511	−138.84821	114	0.08	56	0.27	90

automated EMP and at UoL using a Jeol 8230 Superprobe. Chapman et al. (2010a) reported that the data sets produced using the two analytical facilities are comparable, although the use of the Jeol 8230 Superprobe lowered the limit of detection (LOD) for Hg from 0.3 to 0.06 wt%. The data presented in Table 3 applies the appropriate LOD value to each sample according to their analytical history. All analyses quoted are in weight percent. Mineral inclusions in polished sections were identified through inspection in BSE imaging using the EDS facility of an FEI Quanta 650 FEG-ESEM SEM at UoL. Mineral inclusions in the Bi-Pb-Te-S-Sb system were also analyzed by EMP.

Data presentation

This study considers the significance of the concentrations of Ag, Cu, and Hg in gold alloy. In some cases, the analytical protocol employed included Pd, but this element was not detected and is not considered further. Silver was recorded in virtually all gold particles studied, but Hg and Cu were not always detectable. Tables 2 and 3 (column C) records the percentage of particles within each sample population that contained Hg and Cu to above their detection limits. In some cases, Hg and Cu are present to only just above LOD, whereas in other cases, far higher values were recorded, as indicated by the maximum values presented in Tables 2 and 3 (column M).

The Ag content of gold grain populations is expressed in cumulative percentile plots (e.g., Fig. 3a), which permit direct comparison of compositional profiles of sample populations comprising different numbers of grains. The significance of other minor alloying elements has been established either simply by their concentrations or through their co-variance; for example, Cu-Ag relationships have proved useful in discriminating gold grains derived from porphyry and epithermal environments in the Cyprus-Klaza area. Ternary plots have been used in other compositional studies of natural gold (e.g., Townley et al. 2003) but have not been employed here for comparison, both because the actual data values are lost through normalization and diagrams which feature both Au and Ag effectively plot the same data twice as Ag ≈ (100-Au).

The interpretation of mineral inclusion suites revealed in polished sections of gold grains is a key element of compositional characterization, although reporting this information may be challenging for various reasons. Firstly, the incidence of inclusions varies considerably between localities and is revealed only after completion of the sample collection program. Where possible, this problem can be mitigated by collection of large populations of gold grains, which is more likely to generate a useful inclusion suite, unless gold grains are particularly scarce. Secondly, a large variety of inclusion species may be recorded; for example, in the present study, 22 different opaque mineral species were observed. The combination of low inclusion incidence and a wide number of mineral species is not suited to statistical approaches to characterize data sets. Thirdly, the presence of some individual inclusion species may strongly characterize a particular sample, whereas other minerals such as pyrite are commonly encountered in gold from a range of mineralizing environments. In this study, we have utilized spider diagrams which represent the proportions of different minerals within the overall inclusion assemblage.

Some gold grains exhibited inclusions or coatings of bismuth carbonate, which is the decomposition product of various primary bismuth-bearing minerals. While this feature is very useful in confirming the Au-Bi association, it has not been included in this analysis because (i) it does not indicate a specific primary mineral and (ii) other secondary minerals are not interpreted as indicative of specific un-weathered minerals (e.g., goethite is not assumed to have been derived from pyrite, even though this is probably the case). Data relating to the silver-telluride minerals hessite, (Ag_2Te), petzite, (Ag_3AuTe_2), and cervelleite (Ag_4TeS) has been collated into a single “Ag telluride” category for the purpose of comparing inclusion assemblages between samples.

In two cases (Revenue and Mechanic creeks), data from different sample populations collected at adjacent localities, and which exhibited the same alloy characteristics, have been combined in order to yield an inclusion suite useful for comparative purposes. Details are provided in Table 3.

Results

Composition of gold derived from in situ mineralization

Details of the hypogene ore samples which formed the basis of this study are provided in Table 2.

Nucleus Gold grains from Nucleus ranged in size from 80 to 1000 μm and occur in fractures within pyrite, commonly showing an intimate association with Bi-Te (S) minerals and pyrrhotite, such as that shown in Fig. 2b. Gold particles exhibit a narrow compositional range of between 2.6 and 5.7 wt% Ag (Fig. 3a). Copper was detectable up to values of 0.12 wt%, but Hg was below LOD in around 90% of the gold particles analyzed.

Casino Chapman et al. (2014) identified native gold (5–10 wt% Ag, Fig. 4a), in association with galena, chalcopyrite, sulfosalt, and bismuth-bearing minerals, within a second stage of mineralization in the zone of potassic alteration (Fig. 2c). Detrital grains collected from the leached cap exhibit very similar characteristics (Figs. 2d and 4a).

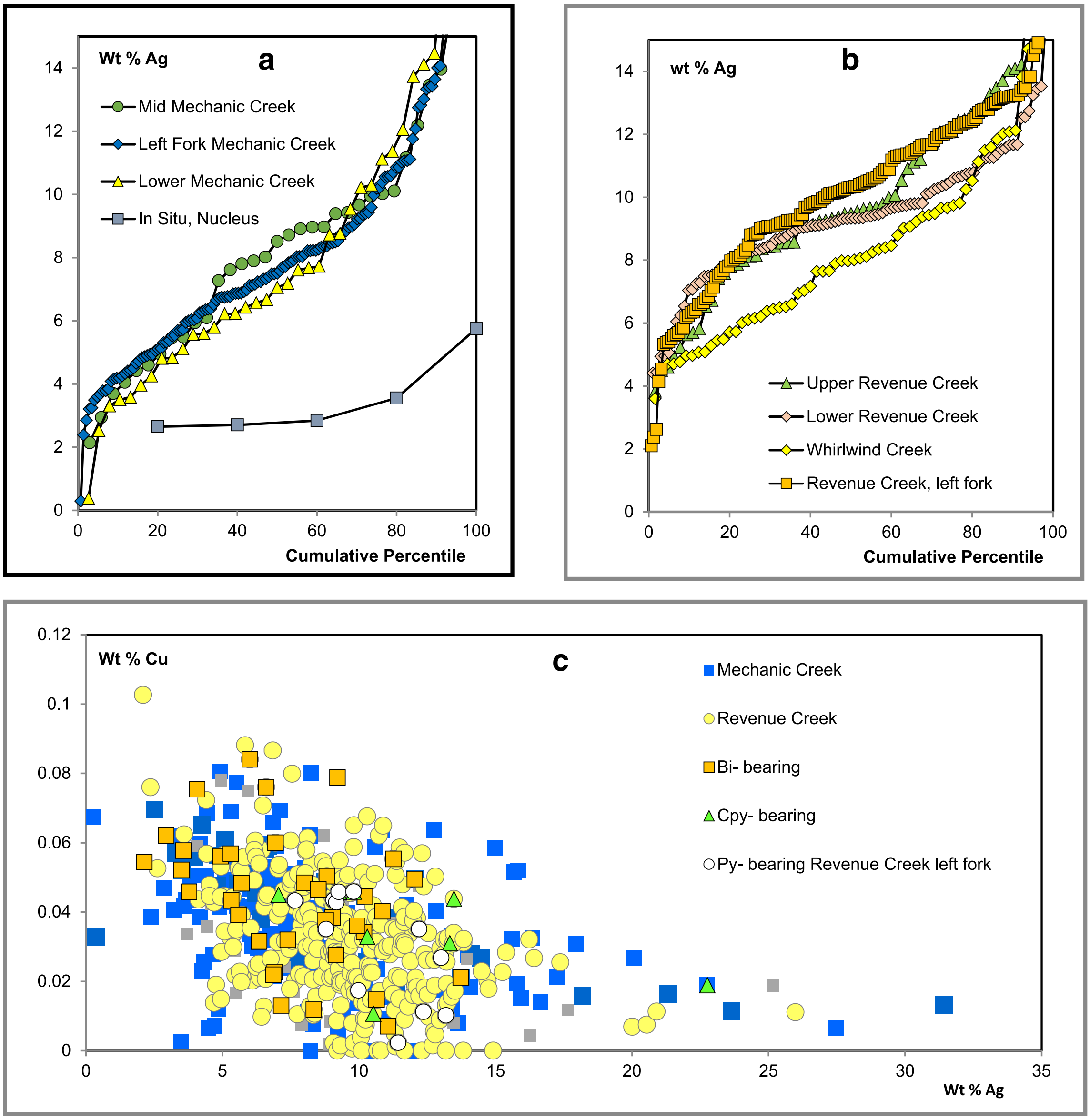

Fig. 3 Alloy compositions and alloy-inclusion relationships in gold particles from Nucleus/Revenue. **a**, **b** Variation in Ag in placer populations from Revenue and Mechanic creeks; **c** covariance of Ag and Cu for placer samples from Revenue and Mechanic creeks specifying host alloy compositions of different inclusion species

Cyprus and Klaza area

No samples of in situ mineralization from Cyprus were available to this study. However, Chapman et al. (2016) concluded that placer gold from Discovery Creek is most probably derived from the adjacent Cyprus porphyry on the basis of sampling locality, gold particle morphology (Fig. 5a) and clast assemblages. Consequently, in the present study, the Discovery Creek sample has been considered equivalent to an eluvial sample derived from porphyry mineralization. The Ag content of these gold grains ranges from 1 to 20 wt% Ag (Fig. 6b). All the grains contained Hg above the LOD but the maximum value was only 0.36 wt% Hg. Eighty percent of grains contained Cu >LOD, to a maximum value of 0.13 wt%. The inclusion assemblage comprised galena, bismuthinite, galenobismutite, and arsenopyrite.

Most of the gold particles identified in core sample 12–96 from Klaza by Chapman et al. (2016) were small (≈2 μm) blebs in pyrite and consequently too small to analyze by EMP, although a later stage gold-galena association was also recorded. The Ag contents of the grains sufficiently large to analyze are illustrated in Fig. 6a, and the co-variance of Ag with Cu and Hg is illustrated in Fig. 6c. Most grains contained detectable Hg, although the maximum concentration was only 0.26 wt%. The ranges of Ag values exhibited by gold in the eluvial samples BRX-1 and BRX-2 are very similar and encompasses the narrower range of Ag values observed in hypogene grains (Fig. 6a). Around 90% of grains from the BRX

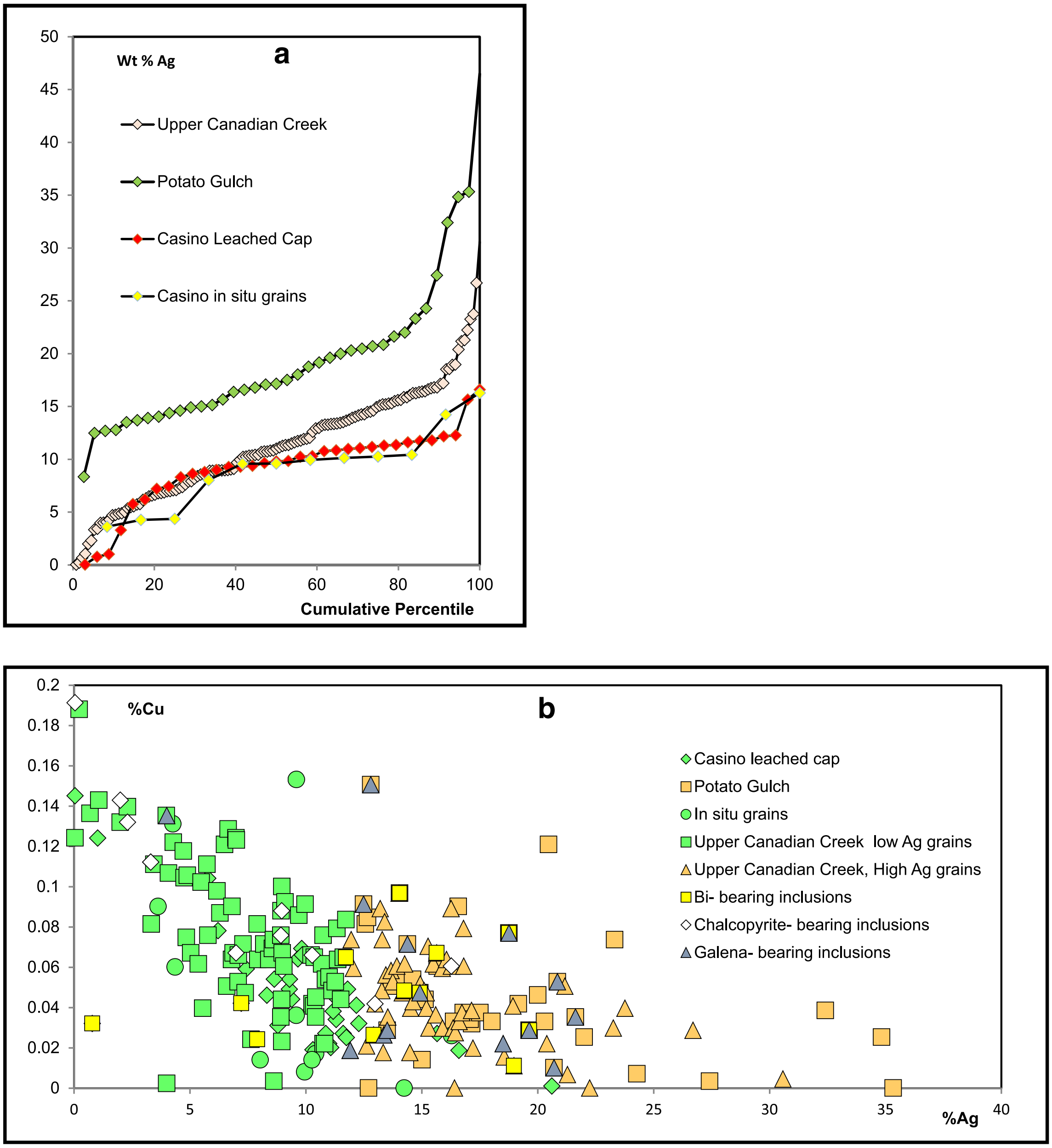

Fig. 4 Alloy and inclusion signatures of samples from the Casino area. **a** Ag contents of in situ, eluvial, and placer gold grains; **b** covariance of Ag and Cu showing compositional fields corresponding to porphyry-derived gold (green symbols) and inferred epithermal gold (orange symbols). Alloy compositions hosting specific inclusions are indicated. Data from Chapman et al. (2014)

zone contain detectable Hg (Table 3), whereas the percentage of grains containing detectable Cu is much lower (35 and 36% in BRX 1 and BRX 2, respectively). Inclusions were scarce, probably as a consequence of the small size of the gold grains, but where present they are compatible with the mineralogy of the hypogene ore; e.g., the galena inclusion illustrated in Fig. 2e.

Characterization of placer samples

Nucleus-Revenue The presence of surface coatings of either bismuth telluride (e.g., Fig. 5b) or its weathered product, bismuthite (BiO_2CO_3) on detrital grains indicates short distances of fluvial transport, as both minerals are very soft. Placer gold samples from different points along Mechanic Creek show a very similar range of Ag contents (Fig. 3a), whereas different Ag signatures were recorded in sample populations collected from the two main tributaries of Revenue Creek (Revenue left fork and Whirlwind creeks, Fig. 3b).

Figure 7a, b compares the mineral inclusion signatures of gold grain populations from the Revenue and Mechanic creek drainages, respectively. The differences in Ag content of the gold from the two tributaries of Revenue Creek is reflected in variations in their inclusion assemblages. Pyrite is the most

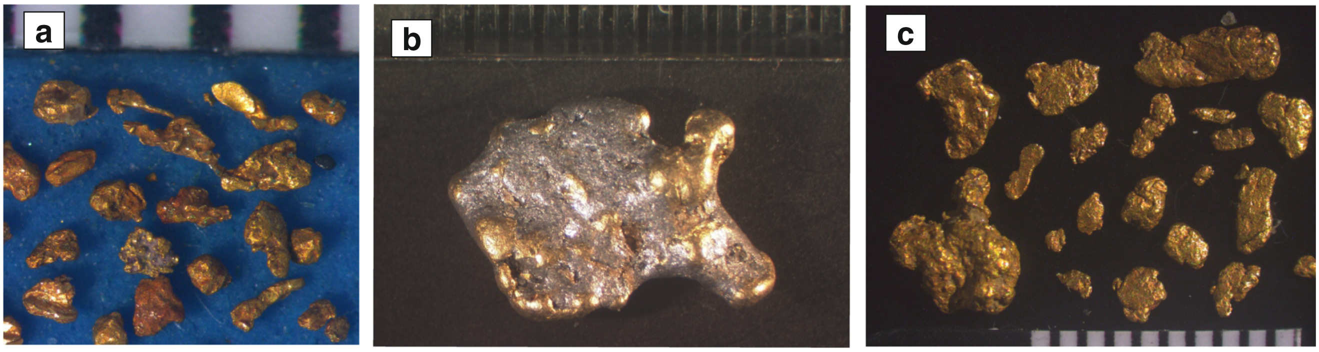

Fig. 5 Morphological characteristics of gold grains which have undergone very limited fluvial transport. **a** Rough small grains from Discovery Creek and Canaan Creek (Klaza); **b** Bi telluride on outside of 10 mm nugget from Mechanic Creek; **c** rough, coarse gold from Potato Gulch, Canadian Creek, Casino. Scale bars on images 1 mm intervals

abundant inclusion in gold from Revenue left fork, whereas only pyrrhotite inclusions were observed in the smaller sample from Whirlwind Creek. All sample populations illustrated in Fig. 7b exhibit a strong Pb-Bi-Te-S inclusion signature. Traces of Sb were detected in many Pb-bearing inclusions but no quantitative information is available. The inclusion signatures of gold from the sampling localities on Mechanic Creek were all very similar. Overall, Pb-bearing minerals are far more common as inclusion species than descriptions of the hypogene mineral assemblage would suggest, but the reasons for this apparent discrepancy are currently unclear.

Co-variance of Ag and Cu is similar for gold particles from localities in this area, but different inclusions occur in alloys of different compositional ranges (Fig. 3c). In general, bismuth-bearing inclusions occur in relatively low-Ag gold alloy which exhibits the full range of Cu values, whereas chalcopyrite-bearing grains exhibit higher Ag contents to a maximum Cu value of 0.06 wt%. Pyrite inclusions were observed only in the sample from Revenue left fork, where their host was also relatively Ag-rich and Cu-poor (Fig. 3c).

Sonora Gulch Only eight grains of placer gold were available to this study, four of which contained inclusions of tetradymite, with another containing chalcopyrite. This data set is too small to plot in Fig. 7, but there is a clear similarity to the Nucleus/Revenue signature in terms of bismuth-bearing inclusions. It seems probable that these grains originate from the “Tetradymite Vein” described by Bennett et al. (2009).

Casino The samples from the Casino area have been previously reported in the study of Chapman et al. (2016). Eluvial gold collected from the leached cap atop the porphyry was characterized by a relatively high Cu, low (< 11.9 wt%) Ag alloy with a strong chalcopyrite association. The placer sample from Potato Gulch 5 km to the north and remote from intrusive rocks yielded gold grains whose morphology suggest a local origin (Fig. 5c). This signature differs from that of the gold collected from the leached cap of the porphyry through a higher Ag content (Fig. 4a), lower Cu content, and an inclusion signature containing Ag tellurides and bismuth-bearing minerals.

Cyprus-Klaza Eluvial gold grains from the BRX zone exhibit a Ag range similar to that of detrital gold from the Canaan Creek placer to the northwest (Figs. 1 and 6a–c), but around 60% of the gold particles from Discovery Creek exhibit Ag contents lower than any grains from the BRX zone (Fig. 6b). The profile of Ag values of gold grains from Nansen Creek (Fig. 6b) suggests multiple influences. Figure 7d shows the inclusion signatures of gold grains from the Klaza veins, Canaan Creek and Nansen Creek. Only seven gold grains from Discovery Creek contained inclusions (four galena, one arsenopyrite, and two bismuth-bearing minerals) and this data set has not been included. Populations of eluvial gold particles from the BRX zones and placer gold particles from Caanan Creek show some similarities in their inclusion signatures, but the placer sample contains Ag-telluride inclusions, which were not observed in the hypogene ore.

Figure 6d permits consideration of the alloy compositions (Ag and Cu) which host inclusion species in both epithermal and porphyry settings. Bismuth-bearing minerals and galena were observed in gold from both styles of mineralization, but additionally, the inclusion suite of the gold from the BRX zones at Klaza corresponded to the vein mineralogy of sphalerite, arsenopyrite, and sulfosalts.

Discussion

Comparison of gold grain inclusions with hypogene ore mineralogy

Previous studies have established the correlation between hypogene gold-bearing mineralization and the suite of inclusions observed within gold grains derived from that mineralization

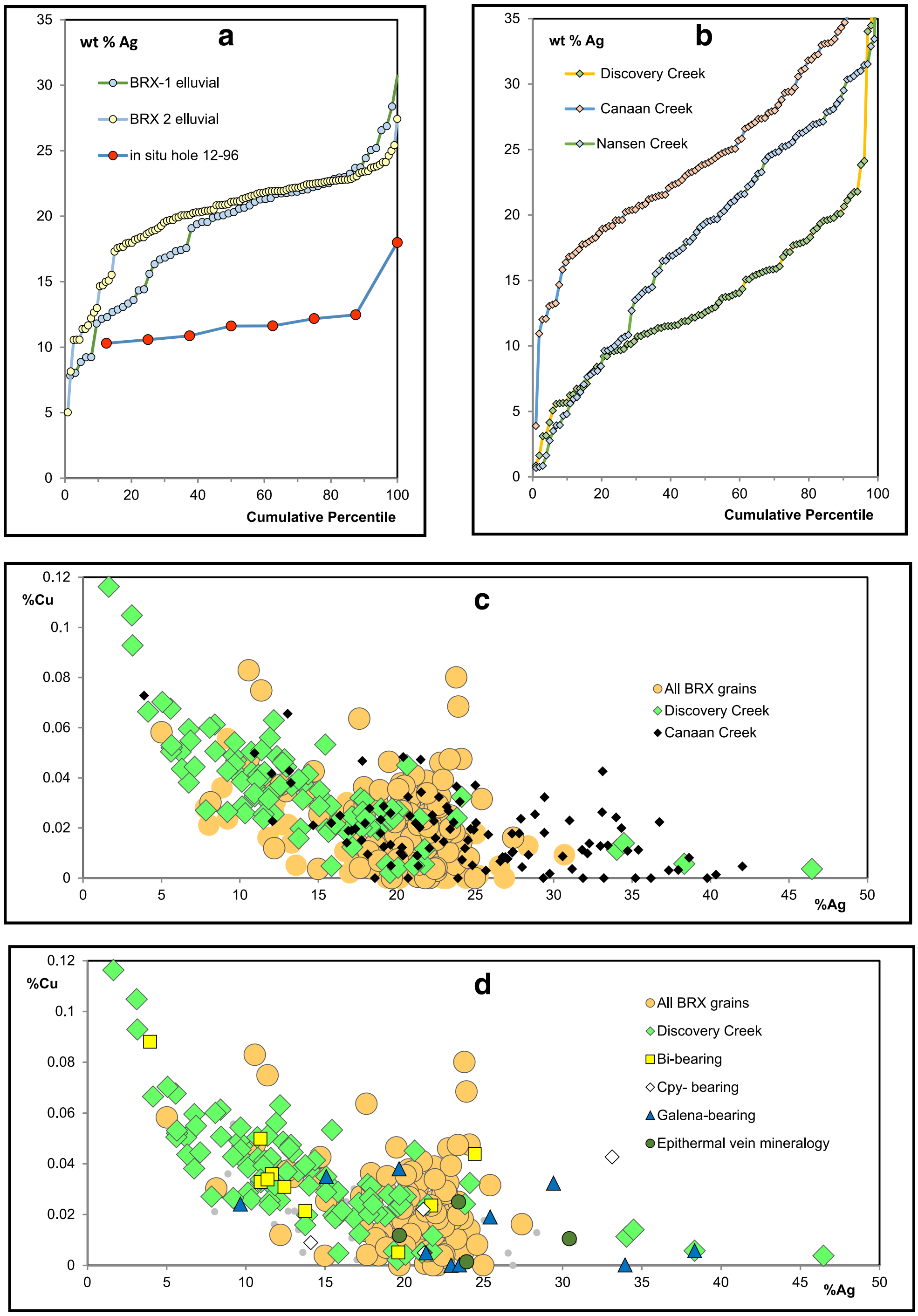

Fig. 6 Characterization of Au alloys from calc alkalic porphyry systems and associated epithermal mineralization. **a** Ag contents of eluvial and hypogene gold particles from the BRX zone, Klaza; **b** Ag contents of placer from, i. Discovery Creek (Cyprus porphyry) (low Ag), ii. epithermal mineralization (high Ag), and a mixture of the two (Nansen Creek); **c** covariance of Cu and Ag in gold from Discovery Creek (Cyprus porphyry) and BRX zone (epithermal) gold at Klaza. Composition of placer gold from Canaan Creek overlaps with BRX zone gold, but extends to higher Ag levels; **d** same but with host alloys of inclusion species from all local placer samples superimposed on compositional fields of gold from Discovery Creek and the BRX Zone. "Epithermal vein mineralogy" comprises inclusions of arsenopyrite, sphalerite, and sulfosalt

(e.g., Chapman et al. 2000, 2017). This general result was replicated in the present study and the associations are summarized below.

The mineral inclusion assemblages in gold from the Casino porphyry and Klaza epithermal veins environments reflect the mineralogy texturally and paragenetically related to gold. At Casino, the mineralogy coeval with gold reported by Chapman et al. (2014) (chalcopyrite, galena, bismuth-bearing minerals, and sulfosalts) is represented in the inclusion signature (Fig. 7c). At Klaza, gold is absent in early pyrite-arsenopyrite mineralization but present in a later stage with galena, sphalerite, and sulfosalts (Chapman et al. 2014). Inclusion mineralogy reflects these associations (Fig. 7d). At both Cyprus/Klaza and Casino, hessite forms an important component of the inclusion assemblages, but it is not observed in the corresponding porphyry samples.

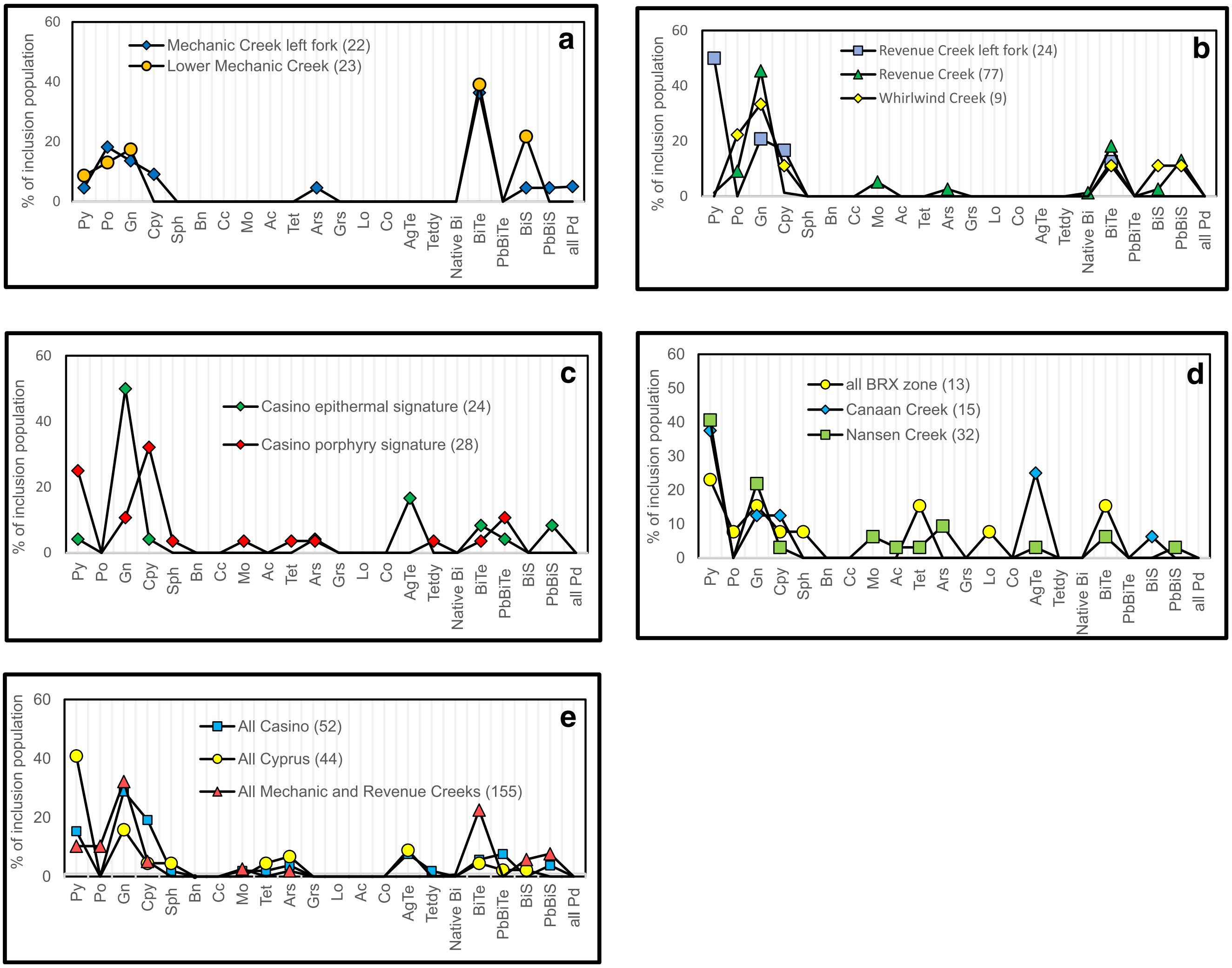

Fig. 7 Depiction of inclusion assemblages. **a** Comparison of placer localities on Mechanic Creek, **b** same for revenue Creek. **c** Signatures of detrital and eluvial gold from Casino, Canadian Creek, and Potato Gulch grouped according to the interpretation of chapman et al. (2014). **d** Comparison of signatures of eluvial gold form epithermal veins at Klaza with gold from adjacent placers. **e** Comparison of detrital gold signatures form all placer localities surrounding Nucleus-Rrevenue, Casino, and Cyprus-Klaza. Figures in parentheses following location identifiers signify the number of gold grains in which inclusions were observed. Key to inclusion species: As for Table 2, plus: Ac=acanthite (Ag_2S) "AgTe" = sum of Ag-Te bearing minerals: hessite, (Ag_2Te), cervelleite, (Ag_4TeS) and petzite,(Ag_3AuTe_2), "All Pd" = all Pd-bearing minerals, Alt= altaite ($PbTe_2$) Apy = arsenopyrite, Bis = bismuthinite (Bi_2S_3), "BiTe" = undifferentiated Bi-tellurides, Cpy = chalcopyrite, Grs= gersdorffite, (Fe,NiAss) Lo = lollingite (FeAs), Mo = molybdenite, , "PbBiS" = undifferentiated Pb-Bi sulfides, PbBiTe' = undifferentiated Pb-Bi tellurides, Py = pyrite, Po = pyrrhotite, Tdy = tetradymite, Bi= native bismuth, Tet = tetrahedrite $(Cu,Fe)_{12}Sb_4S_{13}$)

Comparison of microchemical signatures of gold from different porphyry systems

One aim of the current project is to identify generic features of gold in porphyry systems that may be independent of specific differences in mineralizing processes between sites. Figs. 3, 4, and 6 illustrate the covariance of Ag and Cu at different localities. A general inverse trend between the Ag and Cu content of gold is apparent at both Casino and the Cyprus porphyry (Figs. 4b and 6c). This result is very similar to that reported by Townley et al. (2003), who studied gold alloy compositions of grains from different alteration settings at the Cerro Casale porphyry, Chile. This inverse relationship of Ag and Cu is far less pronounced in the placer sample populations from Revenue and Mechanic creeks (Fig. 3c). The gold mineralization at Nucleus-Revenue is not associated with potassically altered rocks, but the common association of gold with bismuth tellurides both in hypogene ore (Fig. 3b) and placer grains, and the presence of native bismuth (Fig. 2a) could indicate gold concentration by the "Bi-collector model" described above. Ciobanu et al. (2010) suggested an empirically derived relationship between the stoichiometry of bismuth-bearing minerals and the oxidation state of the mineralizing environment. Minerals in which ratios of > 1 were associated with reducing environments, commonly in the presence of pyrrhotite. Analyses of bismuth-bearing mineral inclusions in gold from Mechanic (3), Revenue (3), and Whirlwind creeks (1) revealed average ratios of 1.7, 1.4, and 1.6, respectively. Similarly, analyses of tetradymite inclusions within gold for the Sonora Gulch placer yielded ratios of 1.4. Thus, the mineralogical characteristics of Bi:(Te+S) inclusions in gold from both Nucleus/Revenue and Sonora Gulch are consistent with a relatively reduced intrusion as described by Allan et al. (2013). Betsi and Lentz (2011) presented a paragenesis for the Nucleus deposit which showed a strong Bi-BiS component but not Bi-Te±S minerals reported in the current study. The apparent disparity may be a function of local conditions of mineralization and prevailing *f*Te as suggested by Tooth et al. (2011). In conclusion, it seems likely that the reduced nature of the Nucleus/Revenue intrusion (perhaps a consequence of the assimilation of reduced crust, Betsi and Lentz 2011) explains the importance of the bismuth telluride collector model both here and at Sonora Gulch. Figure 3c shows that for all Nucleus-Revenue samples, the host alloy of chalcopyrite and pyrite inclusions exhibit higher Ag values than the gold associated with bismuth-bearing minerals. This is interpreted as evidence for derivation of some placer grains from the chalcopyrite-pyrite veins described by Allan et al. (2013).

In contrast, there is no compelling evidence for a bismuth collector process at Casino and Cyprus, although the overall elemental signatures of the inclusion suites are similar (e.g., the bismuth telluride inclusion shown in Fig. 3f). Consideration of the mineral inclusion assemblages depicted in Fig. 7c, d shows that the gold-chalcopyrite association observed at Casino is not replicated at Cyprus. This may be a consequence of the obliteration of the original potassic stage ore by a phyllic overprint at Cyprus as described by Hart and Langdon (1997). It seems most likely that the distinctive low-Ag signature of the gold from Discovery Creek corresponds to late stage mineralization within the porphyry, and decomposing in situ arsenopyrite bearing veins were reported here by LeBarge (1995). Placer gold from Nansen Creek (production c. 21,700 oz.; LeBarge 2007) exhibits characteristics common to both gold from Discovery Creek and the epithermal mineralization at Klaza. It appears likely that the gold remobilized from the potassically altered core re-precipitated in mineralized zones originally above the present erosional level.

Mineral inclusion signatures of detrital gold from the Nucleus/Revenue, Cyprus, and Casino porphyry systems are compared in Fig. 7e. There are strong similarities between the systems in terms of the relative abundances of galena, bismuth-bearing minerals, and Sb-As bearing minerals, with the exception that Ag tellurides were not observed at Nucleus-Revenue. In conclusion, although the Bi-Pb-Te-S association in the mineral inclusion suite is most pronounced in gold from Nucleus-Revenue, it is also evident in sample populations from all the other porphyry-related localities studied here.

Evolution of the microchemical signatures of gold in the porphyry-epithermal transition

Mineral inclusion and gold alloy composition data reported in the present study may be compared with gold compositions in the porphyry and epithermal environments reported from other studies and considered with broader considerations of mineralization at specific localities.

There is surprisingly little information available globally as a basis for comparison with the data generated in the present study. Gold alloy compositional data are available, but the methodologies adopted by other workers have not specifically considered mineral inclusions as discriminators of depositional environment. Nevertheless, it is useful to review the available information which is relevant to the new data reported here.

Morrison et al. (1991) considered the alloy compositions of gold formed in both porphyry and adularia-sericite (low sulfidation) epithermal systems. The database describing porphyry deposits was not extensive, and the authors reported variation in Ag ranges at different localities worldwide, while noting that the Cu content of the alloy appeared greater than encountered in gold derived from other deposit types. Both the variation and concentration of Ag in gold from epithermal deposits were greater, for the reasons discussed above.

Controls on Cu in Au-Ag alloy are less clear, but if parallels can be made with the Au-Ag systems developed by Gammons and Williams-Jones (1995), it is reasonable to argue that lower temperature and lower $Cu_{aq}/(Au + Ag)_{aq}$ ratios could lead to lower Cu_{alloy}. However, as discussed previously in relation to the Ag content of gold alloy, metal speciation within hydrothermal regimes at different localities is not always clear, which may result in different compositional trends within the evolving porphyry mineralisation (e.g., at Cerro Casale, Palacios et al. 2001 and Santo Tomas II, Tarkian and Koopmann 1995). While it is at least possible to speculate on the factors affecting the Cu content of Au-Ag alloys, controls on Hg content remain poorly understood (see discussion in Chapman et al. 2010a).

In the present study, consideration of the porphyry-epithermal transition is confined to the Casino and Cyprus porphyry systems. At Cyprus, gold from the Klaza epithermal system has been characterized in detail, but compositional characteristics of gold associated with porphyry mineralization have been inferred from gold collected in an eluvial/placer environment. At Casino, the composition of gold from the porphyry system has been established but the associated epithermal signature has been inferred, through consideration of spatial variations in signatures of placer gold samples (Chapman et al. 2014). Nevertheless, the porphyry-epithermal transition was accompanied by common changes in the microchemical signatures of gold samples, i.e., an increase in Ag content of the alloy and a reduction in Cu content of the alloy. At Cyprus, the trend in Cu contents of gold is sympathetic to a broader change in Cu tenor reported by Hart and Langdon (1997), and Townley et al. (2003) also observed a reduction in the Cu content of native gold with the porphyry epithermal transition at several economically important porphyry and epithermal deposits in Chile and Bolivia. At Casino, gold from the porphyry environment is also distinguished by the far higher incidence of chalcopyrite inclusions (Fig. 7c) than observed in gold from the epithermal environment. While the data set presented here cannot underpin any strong statements about generic changes of microchemical signature in the porphyry epithermal environment, parallel changes have been recorded which are both consistent with observations made by other workers, and broader mineralogical changes associated with evolving magmatic hydrothermal systems.

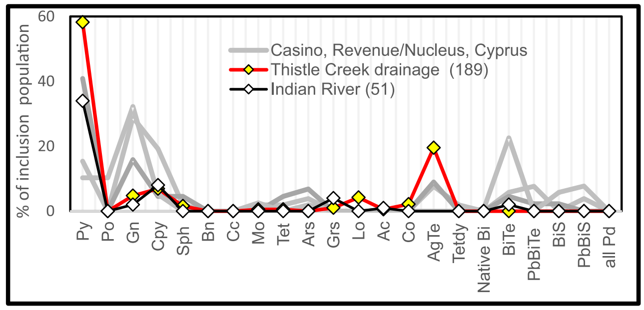

Fig. 8 Comparison of detrital gold signatures from three calc-alkalic porphyry systems with two composite data sets describing inclusion signatures in orogenic gold localities Indian River and Thistle Creek) in the Yukon. Data describing inclusion assemblages of gold from Indian River and Thistle Creek derived from Chapman et al. (2011) and Wrighton (2013), respectively

Implications for exploration

Advances in establishing generic microchemical signature- source relationships

Yukon porphyry systems discussed here all exhibit a common Pb-Bi-Te-S signature in their mineral inclusion suite, even though they show differences in some aspects of their mineralogy. This observation supports our suggestion that the signature may be generic, particularly as the physico-chemical processes responsible for the formation of calc-alkalic porphyry systems are commonly duplicated. At present, focussed studies of gold microchemical signatures in calc-alkalic and associated epithermal systems are lacking, although Chapman et al. (2005) report a strong bismuth telluride inclusion signature associated with Devonian epithermal gold mineralization in central Scotland.

Reviews of the mineralogy of orogenic gold systems also report the presence of bismuth and tellurium minerals (e.g., Goldfarb et al. 2005). In some cases, this association applies to intrusion related systems, and in others to orogenic deposits of Archean age. Studies of gold particles from the Archean granite-greenstone belt of Zimbabwe commonly identified tetradymite inclusions (Styles et al. 1995). Therefore, it is important to make the distinction between the mineralogical characteristics of orogenic gold derived from different metallogenic epochs. The present study has a clear focus on Phanerozoic systems in which both orogenic and porphyry systems may be present.

More information is available on the microchemical signatures of gold from Phanerozoic orogenic mineralization. A summary in Chapman et al. (2009) drew upon multiple examples from the British and Irish Caledonides, Malaysia and early sampling programs in the North American Cordillera. More recent studies of orogenic gold in British Columbia and Yukon (Chapman et al. 2010a, b, 2011, 2016, Wrighton 2013) have reinforced the assertion that although the Ag content of gold formed in orogenic settings may vary considerably, the mineral inclusion signature comprises a relatively simple suite of sulfides, sulfarsenides, and more rarely sulfosalts and tellurides. Where tellurides are observed, they are usually present as hessite, and in all studies in orogenic areas, only a tiny number of gold particles containing bismuth telluride have been reported. Consequently, the mineralogical associations reported here in the Bi-Pb-Te-S system in relation to calc-alkalic porphyry systems of Yukon are a useful discriminant by which to identify gold derived from calc-alkalic porphyry systems as compared to orogenic gold sources.

Chapman et al. (2017) established a strong generic Pd-Hg signature in detrital gold formed in alkalic porphyry systems in British Columbia, which is absent in gold from Yukon calc-alkalic porphyry deposits. Whereas bismuth tellurides were observed as inclusions in detrital gold from alkalic porphyry systems (Chapman et al. 2017) the Bi-Pb-Te-S signature of gold from the calc-alkalic systems described in the present study is far more pronounced. In conclusion, the present study provides powerful additional information to underpin an indicator mineral methodology based on detrital gold.

Practical considerations of developing a gold indicator methodology

Many studies of placer-lode gold relationships rely on gold samples from sites of active or historical placer mining; either from donated samples or simply from the most auriferous strata still present at the site. Such samples cannot be assumed to be fully representative of the lode source(s) from which a placer deposit was derived. The specialized field skills described by Leake et al. (1997) and employed in this study, which are designed to maximize the recovery of gold particles in areas of low overall abundance, should provide more representative samples, and such strategies have successfully underpinned several studies in areas where placer mining is absent (e.g., Chapman et al. 2000).

The majority of studies of placer-lode relationships focus on the replication of the mineralogical features of detrital grains within the gold contained in the hypogene source; however, in the case of porphyry-epithermal systems, it is very likely that gold formed in an epithermal environment may be more commonly encountered, firstly because of a wider geographical footprint (both laterally and from above presently exposed porphyry deposits), and secondly because larger gold particles preferentially accumulate in lag deposits. Consequently, it is necessary to understand the relationship between the microchemical signature of gold from epithermal environments and the gold from related porphyry systems.

Placer-lode relationships in the Dawson Range, Yukon and Alaska

The ability to differentiate between detrital gold particles derived from porphyry or orogenic gold deposit settings is of potential importance in metallogenically diverse areas such as the Yukon-Alaska Cordillera. Economic placer operations are widespread throughout this region, but in many cases, the location and style of the source mineralization remain unclear. The summary of characteristics of gold derived from orogenic settings in Yukon described above has shown that Ag is not particularly useful as a simple discriminant even though it is the most commonly reported characteristic of native gold. Similarly, Hg values in native gold are sporadic and in isolation cannot be used to infer source style, whereas Cu contents of gold may provide some useful information.

Inclusion assemblages provide far more useful information in this regard. Figure 8 illustrates the differences between regional sample sets derived from porphyry and orogenic styles of mineralization. The Indian River composite sample comprises 1311 placer gold grains from 21 localities (Chapman et al. 2011), and the Thistle Creek drainage composite comprises data from 434 grains that were characterized by Wrighton (2013). The sample sets have been chosen as large data sets representing gold derived from orogenic mineralization. The mineralogy of the Bi-Pb-Te-S system present in gold from calc-alkaline porphyry sources presents primarily as minerals containing most or all of these elements (Fig. 8). In contrast, such minerals are either absent or extremely rare in gold form orogenic gold deposit settings, although minerals such as galena or hessite are locally encountered.

Gold grain studies such as this require sufficiently large populations of inclusions to develop robust interpretations. In the example above, one of 51 inclusions observed in gold from the Indian River catchment was a bismuth telluride, but in the large majority of cases, orogenic gold contains no such inclusions. In contrast, between 20 and 40% of inclusions in gold from the porphyry systems studied here are bismuth-bearing minerals. Whereas we cannot state unequivocally that bismuth tellurides and sulphotellurides are diagnostic for porphyry mineralization, the high incidence of such minerals observed here provides a clear indication of the nature of the source.

Conclusions

The technique of "microchemical characterization," in which assemblages of mineral inclusions are established for sample populations of gold grains in tandem with the compositions of their host alloys, enabled discrimination between populations of gold particles derived from different source styles of mineralization. In particular, this approach more clearly discriminates between porphyry, epithermal, and orogenic styles of mineralization than do alloy contents (Ag, Cu, Hg) alone, because alloy compositional ranges commonly overlap between deposit styles.

Gold from four examples of calc-alkaline Cu-Au mineralization in Yukon each exhibit a consistent Bi-Pb-Te-S signature in their mineral inclusion suites despite differences in their overall metal endowment. This common association, together with low but detectable Cu in the alloy, provides criteria by which to distinguish populations of detrital gold particles derived from calc-alkalic porphyry-mineralization from those sourced from other deposit styles in the same geographical region.

In addition, generic changes in the mineralogy associated with the transition from porphyry to low/intermediate sulfidation epithermal mineralization appear to be mirrored in the microchemical signatures of gold from those environments. The Cu signature decreases, both in terms of Cu in gold alloy, and in the abundance of chalcopyrite inclusions, whereas the Ag content of the alloy increases. The Bi-Pb-Te-S mineral inclusion signature in gold from porphyry systems, however, persists into the associated epithermal signature. This observation has important ramifications for exploration, as the footprints of epithermal systems associated with porphyry deposits are commonly present over a wider geographical area than those of related porphyry systems. In conclusion, the clear Pb-Bi-Te-S mineral inclusion signature associated with gold derived from calc alkaline porphyry systems reported here appears to meet the criteria required for a generic indicator. Future studies will seek to confirm the extent to which this approach is globally applicable.

Acknowledgements A large number of companies and individuals have made this study possible. Sampling campaigns around Revenue, Nucleus, Casino, and Klaza would not have been possible without the very positive engagement from Northern Freegold Ltd., Western Copper and Gold

Corp., and Rockhaven Resources Ltd., respectively. Funding for the sampling around Casino and Klaza was obtained from the Yukon Geological Survey as part of the SINED programme. Additional sampling and analysis was facilitated by the Yukon Gold Project, a collaborative research venture between the Mineral Deposit Research Unit of The University of British Columbia and a consortium of industry participants, including Aldrin Resource Corp., Barrick Gold Corp., Full Metal Minerals Corp., Gold Fields Canada Exploration, Northern Freegold Resources Ltd., Kinross Gold Corp., Radius Gold Inc., Silver Quest Resources Ltd., Taku Gold Corp., Teck Resources Ltd., and Underworld Resources Inc. The Yukon Gold Project benefitted enormously from a Collaborative Research and Development grant from the Natural Science and Engineering Research Council of Canada.

Finally, we are extremely grateful for the efforts of the reviewers: Norman Moles and Brian Townley and for the comments of Bernd Lehman, Editor in Chief, which have all greatly enhanced the quality of the manuscript.

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